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(54) Invention Title: Improved Polymerization Method of Olefins

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Specification

1 Invention Title: Improved Polymerization Method of Olefins

2 What is claimed is:

Improved polymerization method of olefins in which at least one of the olefins is polymerized or copolymerized by contacting the olefin(s) with a catalyst comprising

- (A) a catalyst constituent which is obtained by contacting
- (1) a magnesium halide which is treated with an electron donor compound with
- (2) a tetravalent titanium compound containing at least one halogen atom or
- said titanium compound and electron donor compound,
- (B) an organo-aluminum compound,
- (C) an organic carboxylic acid ester
- and
- (D) a compound having a group expressed by M-O-R (wherein M is an element chosen from a group comprising of the IA, IIA, IIB, IIIA, IIIB, IVA and IVB groups in the periodic table, and R is a hydrogen atom or a hydrocarbon group), or a compound expressed by M-O-R (wherein M and R are the same as defined above) and/or oxygen.

3 Detailed Explanation of the Present Invention

[I] Purpose of the Present Invention

The present invention relates to an improved polymerization method of olefins in which a novel catalyst having a very high productivity per unit amount of the catalyst is used to produce polymers having both excellent mechanical properties and plasticity. Describing in more detail, the present invention relates to an improved polymerization method of olefins in which a novel catalyst, which hardly loses its activity even after a comparatively long period of polymerization, is used to produce polymers having very little catalyst residues, excellent mechanical properties and excellent plasticity.

[II] Background of the Present Invention

In recent years, it has come to be considered that a catalyst comprising a solid constituent, in which a titanium compound supports a magnesium halide, and an organo-aluminum compound (hereafter, referred to as "Catalyst A") has a higher polymerization activity than prior art catalysts and may make it unnecessary to remove catalyst residues from produced polymers. However, produced polymers tend to have lower crystallinity and are not satisfactory for use without removing the non-

crystal polymers which exist among the produced polymers. Moreover, the polymerization activity per unit amount of carriers is not satisfactory. Hence, produced polymers tend to contain a relatively large amount of residues of the magnesium halide compound. The residues create disadvantages such as corrosion of polymerization equipment. Other disadvantages include difficulties in production because of the adverse effect on the coloration of produced materials.

The inventors of the present invention conducted research to obtain catalysts which have sufficient polymerization activity to make the removal of catalyst residues and none-crystalline polymers unnecessary and provide sufficiently high three-dimensional regularity in produced polymers. As a result, the inventors found catalysts that provide a very high polymerization activity. Furthermore, the inventors found that surprisingly, when the molecular weight of produced polymers was controlled by hydrogen during the polymerization and polymers having a high melt flow index, no degradation in H.R. was observed. The inventors found that because of this, polymers having a very high three-dimensional regularity can be obtained with a range of MFI (MFI is 1 ~ 20 grams/10 minutes). Such range of MFI can allow for a practical plasticity. The catalysts were previously proposed in the Patent Application Nos. Showa 51-73830, Showa 51-75427, Showa 51-76533, Showa 51-79455 and Showa 51-93948. These catalysts were produced from a solid constituent (A), a trialkylaluminum compound (B), and an organic carboxylic acid ester compound (C). The solid constituent (A) was produced by contacting (1) a magnesium dihalide which was crushed in advance as well as an acyl halide with (2) a mixture of (a) "a tetravalent titanium compound having at least one halogen atom" (hereafter, referred to as "titanium compound") and (b) at least one electron donor compound chosen from a group comprising of ester compounds, organic phosphorous compounds having a P-O bond, organic silicon compounds having a Si-O bond, sulfurous ester compounds, alcohol compounds and phenol compounds, or with an addition reaction compound.

It was found that these catalysts highly improve polymerization activities to the extent that it is unnecessary to remove catalyst residues. It was also found that even when polymers having a practical melt flow index were produced, the three-dimensional specificity was high and moreover, the polymers exhibited practical mechanical properties.

Said catalysts provided excellent effects as described above, when they were used to polymerize olefins. On the other hand, as can be seen quite often with catalysts having a very high polymerization activity, they tend to lose their activity during polymerization, and therefore, the amount of polymers that a unit amount of the catalysts can produce (productivity) remain small. In

other words, these catalysts provide high polymerization activities at the beginning of polymerization whereas the polymerization activities tend to degrade as polymerization progresses and thence, even after a relatively long polymerization reaction duration, the quantity of polymers produced is small. The exact reason of the degradation in the activities is not fully known. It is speculated that reactions between an organo-aluminum compound and an organic carboxylic acid ester compound, which are used to form the catalysts, alter the catalysts.

[III} Design of the Present Invention

Based on the above, the inventors of the present invention conducted various studies on the catalysts which would scarcely show activity degradation during a polymerization process. As a result, the inventors found that said purpose can be achieved by contacting at least one kind of olefin with a catalyst comprising

- (A) a catalyst constituent which is obtained by contacting
 - (1) a magnesium halide which is treated with an electron donor compound with
 - (2) a tetravalent titanium compound containing at least one halogen atomor
said titanium compound and electron donor compound,
 - (B) an organo-aluminum compound,
 - (C) an organic carboxylic acid ester
- and
- (D) a compound having a group expressed by M-O-R (wherein M is an element chosen from a group comprising of the IA, IIA, IIB, IIIA, IIIB, IVA and IVB groups in the periodic table, and R is a hydrogen atom or a hydrocarbon group), or a compound expressed by M-O-R (wherein M and R are the same as defined above) and/or oxygen. Thus, the present invention was accomplished.

[IV] Advantages of the Present Invention

The catalysts of the present invention have a very little degradation in their activities during a polymerization process. Hence, the following advantages are realized when said catalysts are used for olefin polymerization.

The activity does not degrade very much during polymerization. For example, if a catalyst has a half-life of approximately 15 minutes when a three-dimensional specificity is realized without using a compound having an O-R group, or oxygen, then, its half-life is drastically improved by about three times by using a compound having an M-O-R group, and/or oxygen. Thus, as the first advantage, a polymerization process can be carried out for a relatively long duration. Therefore, the productivity of the catalysts is excellent.

When a catalyst of the present invention is used for propylene homopolymerization or copolymerization of propylene and a small amount of another olefin, high-crystallinity polymers can be produced without having to remove polymers having a low melt flow index (hereafter, referred to as "MFI") at a temperature of 230 degrees Celsius and under a load of 2.15 kg or low-crystallinity polymers therefrom and with a high productivity. Such polymers have an MFI value which is suitable for extrusion, hollow formation and so forth.

Moreover, polymers with a relatively high MFI value are very suitable to make films and ejection formation because such polymers are rigid and shows a fluidity during a formation process. When the method of the present invention is implemented, high-crystallinity polypropylene (including copolymers with a small amount of another olefin or ethylene) having a relatively high MFI can be produced without having to remove low-crystallinity polymers therefrom and with a high productivity.

The catalysts of the present invention, which are obtained by choosing each of said catalyst constituents [particularly, the catalyst constituent (A) which is obtained by choosing an electron donor compound], enables polypropylene having the above properties to be obtained without removing catalyst residues and low-crystallinity polymers after the polymerization process. (Polymers with a low MFI value can be also obtained.) In this polymerization method, the following advantages can be realized.

- (1) High-crystallinity polymers with an MFI value in a low range or high range can be obtained without removing catalyst residues and low-crystallinity polymers after the polymerization process. Therefore, polymers having a practical MFI value and moreover, excellent mechanical properties can be produced.
- (2) In particular, during polymers having a practical MFI value range are produced, a very small amount is soluble in the polymerization catalysts. Hence, all of the processing problems are resolved at once, such as attaching themselves to a reaction vessel and a flash hopper, or to each other, and forming lumps. Without going through a process of

removing non-crystal polymers, polymers in a powder form having an excellent fluidity (i.e., powder particles do not stick to each other) can be obtained by simply evaporating the solvent and drying the polymerization solution or polymerization slurry.

- (3) Even when low-crystallinity materials are removed by some method, a very small portion of the desired polymers is soluble in a solvent. Therefore, an ordinarily used solvent is utilized to remove low-crystallinity materials, only a very small amount of the desired polymers is removed and hence, the utilization ratio of the source olefin materials is very high.
- (4) The catalysts of the present invention possess very high polymerization activities. In particular, the polymerization activity per unit amount of a halogenated titanium compound is very high. Halogenated titanium compounds are closely associated with color, odor, and corrosiveness of produced polymers. Without any particular post process to remove or to inactivate catalysts, polymers which are readily suitable for ordinary usage can be easily produced.
- (5) Some polymers are especially required to have as little catalyst residues as possible contained in them. For example, such polymers are used for a stretch forming process. In particular, when such polymers are produced, a polymerization process can be carried out for a relatively long duration so that a higher productivity is achieved. Thus, the purpose is accomplished.
- (6) It is possible to reduce the cost of catalyst production by eliminating a crushing process within the catalyst carrier production.

[V] Concrete Explanation of the Present Invention

(a) Electron Donor Compound

Examples of an electron donor compound used in the present invention include an organic compound having a C-O bond such as an ester compound, a carboxylic acid ester compound, an alcohol compound, a phenol compound, an acetal compound, and an ortho-acid, an organic phosphorous compound having a P-O bond, an organic silicon compound having a Si-O bond, an organic compound having a N-O bond such as a nitrite ester compound, an organic compound having a S-O bond such as a sulfurous ester compound, an acyl halide, and an acid anhydride.

(I) Organic Compound Having a C-O Bond

Among the organic compounds having a C-O bond that can be used in the present invention, examples of an ester compound include a straight or branched ester having at most 40 carbon atoms and having an aliphatic, alicyclic or aromatic hydrocarbon group(s), which may be partially substituted with a halogen(s). Among these ester compounds, those which can be expressed by general formula, $R-O-R'$, is preferred, wherein R and R' may or may not be identical, and each is a group having at most 12 carbon atoms. Representative examples of these preferred ester compounds include diethyl ester, di-n-propyl ester, di-isopropyl ester, di-n-butyl ester, di-isobutyl ester, anisole, ethoxybenzene and diphenyl ester.

Among the organic compounds having a C-O bond, examples of a carboxylic acid ester compound that is used in the present invention include a carboxylic acid ester which is derived from an aliphatic, alicyclic or aromatic carboxylic acid having at most 20 carbon atoms and an aliphatic, alicyclic or aromatic, monohydric or polyhydric alcohol having at most 20 carbon atoms, wherein such an carboxylic acid is partially substituted with at most 3 halogen atoms or alkoxy groups.

Among these organic carboxylic acid ester compounds, aromatic carboxylic acid ester compounds are particularly preferred. Representative examples of preferred organic carboxylic acid ester compounds include methyl benzoate, ethyl benzoate, n-propyl benzoate, isopropyl benzoate, butyl benzoate, octyl benzoate, cyclohexyl benzoate, phenyl benzoate, methyl toluate, ethyl toluate, methyl anisate, dimethyl phthalate, diethyl phthalate, diethyl terephthalate, ethyleneglycol benzoate, and methyl naphthoate.

Among the organic compounds having a C-O bond, examples of an alcohol compound include monohydric or polyhydric alcohol. Particularly preferred alcohol compounds are monohydric or polyhydric alcohol compounds having 2 to 20 carbon atoms and having a hydrocarbon group(s) chosen from a group comprising of an alkyl group, a cycloalkyl group, and an aralkyl group, and said hydrocarbon group(s) substituted with a halogen atom(s) and/or an alkoxy group(s). Representative examples of the preferred alcohol compounds include ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec butyl alcohol, tert-butyl alcohol, isoamyl alcohol, cyclohexanol, stearyl alcohol, benzyl alcohol, ethyleneglycol, propyleneglycol, and glycerin.

Among the organic compounds having a C-O bond, preferred phenol compounds have at most 20 carbon atoms and are phenol and naphthol which are unsubstituted or substituted with an alkyl group(s), an alkoxy group(s) and/or a halogen atom(s). Representative examples of preferred phenol

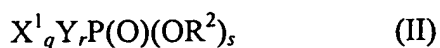
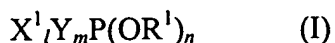
compounds include phenol, m-cresol, p-cresol, p-methoxyphenol, p-tert-butylphenol, 2,6-dimethylphenol, and β -naphthol.

Among the organic compounds having a C-O bond, acetal compounds are those which are driven from the above-mentioned alcohol compounds, aldehydes having at most 20 carbon atoms, or ketones having at most 20 carbon atoms and include hemiacetal. Representative examples of such acetal compounds include ethylal, acetal, acetonediacetal, and benzaldehydediacetal.

Among the organic compounds having a C-O bond, an ortho-acid ester compound is derived from a carboxylic acid having at most 10 carbon atoms and an alcohol having at most 10 carbon atoms. Representative examples of such an ortho-acid ester compound include ethyl-ortho-formate, and ethyl-ortho-acetate.

(II) Organic Phosphorous Compound Having a P-O Bond

Among the organic phosphorous compounds having a P-O bond (hereafter, referred to as "organic compounds containing phosphor") which are used in the present invention, representative ones are expressed by the general formulae below.



In formulae (I) and (II), the sum of l , m and n is 3 and the sum of q , r and s is also 3, wherein $0 \leq l, m < 3$, $0 < n \leq 3$, $0 \leq q, r \leq 3$ and $0 \leq s \leq 3$. R^1 and R^2 may or may not be identical. Each of them is chosen from a group of hydrocarbons comprising saturated or unsaturated aliphatic, alicyclic and aromatic hydrocarbon groups having at most 20 carbon atoms, which may or may not be substituted with a halogen atom(s) or an alkoxy or aryloxy substituent(s) having at most 20 carbon atoms. X^1 and Y may or may not be identical. They are chosen from a hydrogen atom, a halogen atom, a hydroxyl group, and the above-mentioned (saturated or unsaturated, and substituted or unsubstituted) hydrocarbon groups.

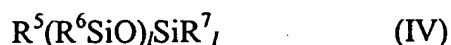
Representative examples of organic compounds containing phosphor which are expressed by formula (I) include ethyldiacetylphosphinite, ethylbutylethylphosphinite, ethylphenylmethylphosphinite, butylphenylbiphenylphosphinite, phenyldibenzylphosphinite,

dimethylethylphosphinite, diphenylethylphosphinite, diethylbenzylphosphinite, diphenylethylphosphinite, diethylbenzylphosphinite, diethyl-2-chloroethylphosphinite, trimethylphosphite, triethylphosphite, tri-n-propylphosphite, tri-isopropylphosphite, tri-allyl-phosphite, tri-n-butylphosphite, triphenylphosphite, tricyclohexylphosphite, tribenzylphosphite, tris(3-ethoxypropyl)phosphite, tris(2-chloroethyl)phosphite, tricresylphosphite, diphenylnonylphenylphosphite, tris(nonylphenyl)phosphite, diphenylisodecylphosphite, triisodecylphosphite, tris(2-ethylhexyl)phosphite, ethylethylphosphonochloridite, phenylethylphosphonochloridite, phenylphenylphosphonochloridite, n-butylphenylphosphonochloridite, diethylchlorophosphite, diphenylchlorophosphite, dioctylchlorophosphite, diethylbromophosphite, dibenzylchlorophosphite, benzylchlorophosphite, 2-chloroethyldichlorophosphite, and hexyldichlorophosphite.

Representative examples of organic compounds containing phosphor which are expressed by formula (II) include methyldimethylphosphinate, methyldiethylphosphinate, ethyldiethylphosphinate, ethyldipropylphosphinate, ethyldi-n-butylphosphinate, ethyldiphenylphosphinate, methyldicyclohexylphosphinate, 2-chloroethyldibenzylphosphinate, ethylethylphosphonochloridate, phenylethylphosphonochloridate, phenylphenylphosphonochloridate, n-butylphenylphosphonochloridate, ethylethylphosphonobromidate, diethylmethylphosphonate, diphenylphenylphosphonate, dioctylbutylphosphonate, diethylphenylphosphonate, diallylphenylphosphonate, bis(2-chloroethyl)phenylphosphonate, diethylcyclohexylphosphonate, diethylbenzylphosphonate, diethylphosphochloridate, di-n-butylphosphochloridate, dioctylphosphochloridate, diphenylphosphochloridate, dibenzylphosphochloridate, dicresylphosphochloridate, bis(2-chloroethyl)phosphochloridate, diphenylphosphobromidate, ethylphosphodichloridate, n-butylphosphodichloridate, phenylphosphodichloridate, benzylphosphodichloridate, cresylphosphodichloridate, ethylphosphodibromidate, triethylphosphate, tri-n-butylphosphate, triphenylphosphate, tribenzylphosphate, trihexylphosphate, diethylphosphate, di-n-butylphosphate, diphenylphosphate, cresyldiphenylphosphate, tricresylphosphate, tritolylphosphate, trixylylphosphate, diphenyl-mono-O-xenylphosphate, diphenylxenylylphosphate, tris(bromo-chloropropyl)phosphate, triethylphosphin oxide, tri-n-butylphosphin oxide, and triphenylphosphin oxide.

(III) Organic Silicon Compound Having a Si-O Bond

Among the organic silicon compounds having a Si-O bond (hereafter, referred to as "silicon compounds") which are used in the present invention, representative ones are expressed by the general formulae below.



In formulae, R^3 is a hydrocarbon group having at most 20 carbon atoms which is chosen from a group comprising an alkyl group, cycloalkyl group, an aryl group or aralkyl group, wherein these hydrocarbons may or may not be saturated, and may or may not be substituted with a halogen atom(s) or an alkoxide(s) having at most 20 carbon atoms. R^4 , R^5 , R^6 , R^7 , and R^8 may or may not be identical. Each of them is one of the above hydrocarbons, which may be substituted, a hydrogen atom or a halogen atom. The value of $m + n$ is 4 while m is not 0, l is an integer from 1 to 1,000, and p is an integer from 2 to 1,000.

Representative examples of silicon compounds which are expressed by formula (III) include tetramethoxysilane, dimethyldimethoxysilane, tetraethoxysilane, triethoxyethylsilane, diethoxydiethylsilane, ethoxytriethylsilane, tetrapropoxysilane, dipropoxydipropylsilane, tetra-isopropoxysilane, di-isopropoxy-di-isopropylsilane, dimethoxydiethylsilane, diethoxydibutylsilane, tetra-n-butoxysilane, di-n-butoxy-di-n-butylsilane, tetra-sec-butoxysilane, tetrahexosilane, tetraoctoxysilane, trimethoxychlorosilane, dimethoxydichlorosilane, dimethoxydibromosilane, triethoxychlorosilane, diethoxydibromosilane, dibutoxydichlorosilane, dicyclopentoxydiethylsilane, diethoxydiphenylsilane, 3,5-dimethylphenoxytrimethylsilane, methylphenyl-bis(2-chloroethoxy)silane, dimethoxydibenzylsilane, tri-n-propylallyloxysilane, allyltris(2-chloroethoxy)silane and trimethoxy-3-ethoxypropylsilane.

Representative examples of silicon compounds which are expressed by formula (IV) include hexamethyldisiloxane, decamethyltrisiloxane, tetracosamethylundecasiloxane, decamethyltrisiloxane, tetracosamethylundecasiloxane, 3-hydroheptamethyltrisiloxane, hexaphenyldisiloxane, hexacyclohexyldisiloxane, 1,3-dimethyldisiloxane, octaethyltrisiloxane, hexapropyldisiloxane, 1,3-

dichlorotetramethyldisiloxane, 1,3-bis(p-phenoxyphenyl)-1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-diallyltetramethyldisiloxane, 1,3-dibenzyltetramethyldisiloxane, 2,2,4,4-tetraphenyl-2,4-disila-1-oxacyclopentane, 1,1,3,3-tetramethyldisiloxane, and hexachlorodisiloxane.

Representative examples of silicon compounds which are expressed by formula (V) include 1,3,5-trimethylcyclotrisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, pentamethylchlorocyclotrisiloxane, 1,3,5-trimethyltriphenylcyclotrisiloxane, hexaphenylcyclotrisiloxane, 1,3,5-tribenzyltrimethylcyclotrisiloxane, 1,3,5-triallyltrimethylcyclotrisiloxane, and hydromethylpolysiloxane.

Among these silicon compounds, preferred ones are polysiloxane which has a viscosity of 10 to 500,000 centistokes at 25 degrees Celsius and alkoxysilane. Particularly preferred ones are tetramethoxysilane, tetraethoxysilane, dimethyldimethoxysilane, diethyldiethoxysilane, methoxytrimethylsilane, trimethoxymethylsilane, hexamethyldisiloxane, octamethyltrisiloxane, dimethylpolysiloxane, and phenylmethylpolysiloxane.

(IV) Organic Compound Having a N-O or S-O Bond

Examples of an organic compound having a N-O or S-O bond that are utilized in the present invention include nitrous ester compounds and sulfurous ester compounds.

Examples of such nitrous ester compounds and sulfurous ester compounds include nitrous ester compounds and sulfurous ester compounds having a hydrocarbon group(s) chosen from a group comprising of an allyl group, a cycloalkyl group, an aryl group, and an aralkyl group which have at most 8 carbon atoms. In particular, nitrous ester compounds and sulfurous ester compounds having an aralkyl group(s) having at most 8 carbon atoms are preferred. Examples of such particularly preferred nitrous ester compounds and sulfurous ester compounds include methyl nitrite, ethyl nitrite, butyl nitrite, isoamyl nitrite, dimethyl sulfite, and diethyl sulfite.

(V) Acyl Halide

A general formula of representative examples of an acyl halide which is utilized as an electron donor compound in the present invention is expressed by the formula below, (VI).

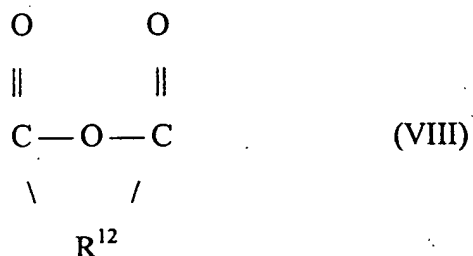
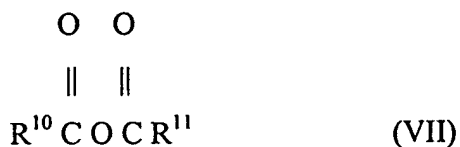




In formula (VI), R^9 is a saturated or unsaturated aliphatic, alicyclic or aromatic hydrocarbon group having at most 20 carbon atoms, or said hydrocarbon group substituted with a halogen atom(s) or an alkoxy group(s). X^2 is a halogen atom. Among such acyl halides, aromatic carbonyl halides are preferred. Benzoyl chloride, benzoyl bromide, toloyl chloride, and toloyl bromide are more preferred.

(VI) Acid Anhydride

A general formula of representative examples of an acid anhydride halide which is utilized as an electron donor compound in the present invention is expressed by the formulae below, (VII) and (VIII).



In formulae (VII) and (VIII), R^{10} and R^{11} may or may not be identical, and each of them is an aliphatic, alicyclic or aromatic hydrocarbon group having at most 20 carbon atoms, or said hydrocarbon group substituted with at most 10 halogen atoms. R^{12} is an aliphatic, alicyclic or aromatic hydrocarbon group having at most 20 carbon atoms, or said hydrocarbon group substituted with at most 10 halogen atoms.

Among such acid anhydrides, aromatic carboxylic acid anhydrides, such as benzoic anhydride and phthalic anhydride, and aliphatic carboxylic acid anhydrides having at most 40 carbon atoms, such as propionic anhydride and acetic anhydride.

(VII) Other Electron Donor Compounds

Examples of electron donor compounds other than the above include ketone compounds such as dibutylketone, and cyclohexanone, aldehyde compounds such as butylaldehyde and benzaldehyde, carboxylic acid compounds such as stearic acid and benzoic acid, amine compounds such as tributylamine, diphenylamine, γ -picoline and morpholine, boric acid ester compounds such as triethoxyboron, titanate compounds such as tetraethyl titanate and tetrabutyl titanate, and aluminumalkoxide compounds such as triethoxyaluminum and tributoxyaluminum.

(b) Magnesium Dihalide

Magnesium dihalides which are utilized in the present invention do not contain crystallization water. They are so-called anhydrides. When a commercially available material is purchased, it is generally desirable to dry the material at 200 ~ 630 degrees Celsius. Representative examples are magnesium chloride, magnesium bromide, and magnesium iodide. In particular, magnesium chloride is preferred.

(c) Treatment of an Electron Donor Compound and Magnesium Dihalide

Examples of treatment methods of an electron donor compound and magnesium dihalide include the following methods. In one method, an electron donor compound and magnesium dihalide are mixed and contacted. In another method, magnesium dihalide in a powder form is added to a solution containing an electron donor compound and the solution is then stirred. In a third example method, ultra sound is irradiated to a mixture of an electron donor compound and magnesium dihalide. In another method, a mixture of an electron donor compound and magnesium dihalide is crushed. In particular, the method in which the materials are crushed produces an excellently treated material and is preferred.

A treatment temperature is in general, in a range from room temperature (15 degrees Celsius) to 350 degrees Celsius. A treatment temperature in a range from room temperature to 250 degrees Celsius is preferred. A treatment temperature in a range from room temperature to 150 degrees Celsius is more preferred. If a treatment temperature is 350 degrees Celsius or higher, the three-dimensional specificity of an obtained catalyst degrades and hence, is not preferred. On the other hand, if a treatment temperature is room temperature or lower, then the polymerization activity of an obtained

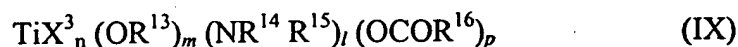
catalyst solid constituent degrades and the amount of ash in polymers to be produced would increase. Hence, this temperature range is not preferred, either.

The ratio between an electron donor compound and magnesium dihalide to be treated shall be in general, such that in a treated mixture, the mole ratio of electron donor compound (when this compound is a polymer, then the amount of constituent monomers in mole – this applies in all cases hereafter) and magnesium atoms becomes 0.01 to 2. In particular, a mole ratio of 0.01 to 1.5 is preferred. Practically speaking, when this mole ratio is too large, the activity of an obtained catalyst becomes low. On the other hand, a low mole ratio results in an insufficient three-dimensional specificity of an obtained catalyst.

A treated material which is obtained as described above from an electron donor compound and magnesium dihalide tend to form larger lumps as a larger amount of the electron donor compound is used compared to that of the magnesium dihalide and as the treatment temperature is increased. Therefore, in order to obtain a catalyst having a convenient dimension for a practical use, such a treated material shall be preferably crushed or ground into powder having particles of 1 mm (more preferably 0.2 mm) or less in diameter. When a crushing method is utilized to treat an electron donor compound and magnesium dihalide, then a subsequent crushing process is not necessary. Hence, such a method is preferred.

(d) Titanium Compound

Furthermore, a titanium compound which is utilized in the present invention has at least one halogen atom and is tetravalent. It is expressed by a general formula (IX) below.



In formula (IX), X^3 is a chlorine, bromine or iodine atom, and R^{13} , R^{14} , R^{15} , and R^{16} are aliphatic, alicyclic or aromatic hydrocarbon groups having at most 12 carbon atoms. In the formula, n is a number from 1 to 4, m , l and p are numbers from 0 to 3, and $n + m + l + p = 4$. It is preferred that n satisfies $n \geq 3$. Particularly, it is more preferred that m is in a range from 0 to 1 while n satisfies $n \geq 3$. Representative examples of preferred titanium compounds include titanium tetrahalide, and alkoxytitanium halides. In particular, titanium tetrachloride, methoxytitanium trichloride, and ethoxytitanium trichloride are preferred.

(e) Production of Catalyst Constituent (A)

The titanium compound alone may be used to produce catalyst constituent (A) of the present invention. However, it is preferred to use one of the above-mentioned electron donor compounds as well as said titanium compound because that will improve the three-dimensional specificity of the produced catalyst. If one compound from "ester compounds, organic compounds having a C-O bond excluding acid anhydrides, organic compounds containing phosphor, silicon compounds or compounds having a S-O bond" (hereafter referred to as "C-group electron donor compounds") is used to produce a treated material from said magnesium dihalide and an electron donor compound (hereafter, referred to as "electron donor compound (A)"), it is preferred that preparation of catalyst constituent (A) by contacting said treated material with a titanium compound and an electron donor compound (hereafter referred to as "electron donor compound (B)") is done using one of the following: "acyl halides, acid anhydrides and silicon compounds" (hereafter, referred to as "D-group electron donor compounds"). On the other hand, if one compound from the D-group electron donor compounds is used as electron donor compound (A), it is preferred that one compound from the C-group electron donor compounds is used as electron donor compound (B). These choices are preferred from the view point of the polymerization activity. In particular, these are preferred for homopolymerization of propylene or copolymerization of propylene with a small amount of other olefins. This is because obtained polymers exhibit an excellent three-dimensional specificity even if they have a high MFI value. (Of course, obtained polymers exhibit an excellent three-dimensional specificity when they have a low MFI value.) Preferred compounds among C-group electron donor compounds are organic compounds containing phosphor, silicon compounds, ester compounds, nitrite ester compounds, sulfurous ester compounds, and alcohol compounds. Organic compounds containing phosphor, silicon compounds, ester compounds having an aromatic ring(s), nitrite ester compounds, and sulfurous ester compounds are especially more preferred. Among D-group electron donor compounds, acyl halides are preferred.

Catalyst constituent (A) can be obtained by contacting the above-mentioned titanium compound, or said compound and electron donor compound (B) with "a treated material of the above-mentioned electron donor compound (A) and magnesium halide" (hereafter, referred to as "constituent (1)"). This contact treatment does not require a special process. Examples of the treatment include the methods below.

- (1) A method in which constituent (1) is submersed in a solution in which a titanium compound or said compound and electron donor compound (B) are dissolved.
- (2) A method in which constituent (1) is submersed in a solution of a titanium compound in advance and subsequently, electron donor compound (B) is added to the solution so that a contact treatment takes place with a simultaneous presence of the three materials.
- (3) A method in which constituent (1) is submersed in a solution of electron donor compound (B) in advance and subsequently, a titanium compound is added to the solution so that a contact treatment takes place with a simultaneous presence of the three materials.
- (4) A method in which constituent (1) and a titanium compound, or the three materials are simultaneously crushed or ground.
- (5) A method in which an adduct product of electron donor compound (B) and a titanium compound is ground or crushed together with constituent (a).
- (6) A method in which constituent (1) is treated with electron donor compound (B) using one of the methods above and then the processed materials are treated with a titanium compound using one of the methods above.
- (7) A method in which constituent (1) is treated with a titanium compound using one of the methods above and then the processed materials are treated with electron donor compound (B) using one of the methods above.

The amount of electron donor compound (B) is in general at most 20 moles to 1 mole of a titanium compound. Preferably, the amount of electron donor compound (B) should be 10 moles or less to 1 mole of a titanium compound. In particular, 0.5 to 5 moles is more preferable because a large amount of quantitatively balanced compounds between a titanium compound and electron donor compound (B) can be formed in this range. When the amount of electron donor compound (B) exceeds 20 moles to 1 mole of a titanium compound, the polymerization activity of a catalyst to be produced for a unit amount of titanium becomes low, which is not desirable.

As for a contact treatment, constituent (1) and a titanium compound, or said compound and electron donor compound (B) can be contacted. When a titanium compound and electron donor compound (B) come in contact with each other simultaneously, it is preferred that both materials are put in a solvent which is then stirred, or the materials are placed in a crushing machine, where they are

crushed together. By doing so, the treatment can be performed efficiently. Examples of solvents in which a titanium compound and acyl halide are mixed or reacted, or stirred for a contact treatment include aliphatic hydrocarbons such as hexane, heptane, octane and ligroin, aromatic hydrocarbons such as benzene, toluene and xylene, and halogenated hydrocarbons such as methylene chloride, trichloroethane, trichloroethylene, and chlorobenzene. When a solution is stirred for a contact treatment, the more concentrated the solution is, the more preferred, as long as the concentration does not interfere with the treatment. Normally, a concentration is 0.005 mole of Ti/liter or higher.

The temperature for a contact treatment is in general -10 to $+200$ degrees Celsius. At a lower temperature, the polymerization activity exhibited by a catalyst will be low. On the contrary, at a higher temperature, the three-dimensional regularity of produced polymers will be low. Hence, to obtain the best results, a temperature of 20 to 180 degrees Celsius is desired.

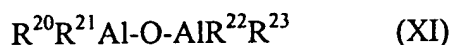
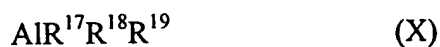
A contact treatment is normally carried out for 10 minutes or longer. A sufficient amount of a catalyst constituent will be supported on carriers in approximately 2 hours. No improvements were observed when a contact treatment was carried out for more than 10 hours.

It is preferred that the produced polymers are washed in an inert solvent (e.g. an aromatic hydrocarbon used as a solvent in a contact treatment by stirring) after the contact treatment.

When a contact treatment is performed through crushing source materials without using a solvent, a preferred amount of a titanium compound is $1 \sim 1/1,000$ parts per part of constituent (1) in weight. In particular, an amount of $1/3 \sim 1/300$ parts per part of constituent (1) in weight is more preferred. When 1 mole or more of a titanium compound is crushed with one part in weight of constituent (1), many of the obtained catalyst particles tend to attached themselves to each other very easily. Hence, this ratio is not preferred. On the other hand, when $1/1,000$ parts in weight of a titanium compound is crushed with one part in weight of constituent (1), the prepared catalyst exhibit a very low polymerization activity. Hence, this ratio is not preferred. A contact treatment, such as crushing, may be performed under the presence of a solvent. Purposes of a solvent usage include preventing source material particles from attaching themselves to each other. Then, the amount of a titanium compound may be allowed to increase to as large as 50 parts in weight per part in weight of constituent (1).

(f) Organo-Aluminum Compound

Representative examples of an organo-aluminum compound which is used in combination with the catalyst constituent prepared by the above process of the present invention is expressed by general formulae (X), (XI) and (XII) below.



In formula (X), R^{17} , R^{18} and R^{19} may or may not be identical. Each of them is a hydrocarbon group having at most 12 carbon atoms, a halogen atom, or a hydrogen atom. However, at least one of the three is a hydrocarbon group. In formula (XI), R^{20} , R^{21} , R^{22} and R^{23} may or may not be identical. Each of them is a hydrocarbon group having at most 12 carbon atoms. R^{24} is the previously-mentioned hydrocarbon group and X^4 is a halogen atom.

Representative examples of an organo-aluminum compound which is expressed by formula (X) include trialkylaluminum such as triethylaluminum, tripropylaluminum, tributylaluminum, trihexylaluminum and trioctylaluminum, alkylaluminumhydride such as diethylaluminumhydride and diisobutylaluminumhydride, diethylaluminum chloride and diethylaluminum bromide.

Representative examples of an organo-aluminum compound which is expressed by formula (XI) include alkylalumoxane such as tetraethyldialumoxane and tetrabutylalumoxane. Moreover, representative examples of an organo-aluminum compound which is expressed by formula (XII) include ethylaluminum sesquichloride

Among these organo-aluminum compounds, trialkylaluminum and alkylalumoxane are preferred. In particular, triethylaluminum, triisopropylaluminum, tributylaluminum, and tetraethyldialumoxane are preferred.

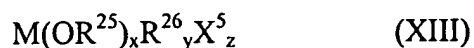
(g) Organic Carboxylic Acid Ester.

An organic carboxylic acid which is used in the present invention can be selected among those which are shown for C-group electron donor compound in the above. Among these organic carboxylic acid esters, an aromatic carboxylic acid ester compound is preferred. A particularly preferred one is

obtained from an aromatic carboxylic acid having at most 12 carbon atoms and a monohydric aliphatic alcohol having 12 or less carbon atoms. Representative examples of the preferred organic carboxylic ester include methyl benzoate, ethyl benzoate, methyl anisate, methyl toluate and ethyl toluate.

(h) Compound Having an M-O-R Group

Representative examples of a compound having an M-O-R group which is used in the present invention is expressed by a general formula (XIII) below.



In formula (XIII), M represents an element chosen from a group comprising elements of the IA, IIA, IIB, IIIA, IIIB, IVA and IVB groups of the periodic table. R^{25} and R^{26} may or may not be identical. Each of them is a hydrogen atom, or a hydrocarbon group having at most 18 carbon atoms which is chosen from a group comprising an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group and an aralkyl group. X^5 is a halogen atom. Furthermore, the sum, $x + y + z$, is equal to the valence of atom M, wherein x is larger than 1. Among the compounds expressed by the formula, those are preferred in which M is chosen from a group comprising H, Li, Na, K, Mg, Ca, Sr, Ba, Zn, B, Al, Sc, Ga, Si, Ge, Sn, Ti and Zr, and z is equal to or less than 1. In particular, those are more preferred in which M is chosen from a group comprising H, Mg, Al and Si, R^{25} is a hydrocarbon group having at most 8 carbon atoms, R^{26} is a hydrocarbon group having at most 8 carbon atoms and z is equal to or less than 1.

Among such compounds having an M-O-R group, preferred representative examples include water, metal hydroxides such as magnesium hydroxide, aluminum hydroxide, diethyldihydroxysilane, trimethylhydroxysilane and triphenylhydroxysilane, metal alkoxides such as magnesiummethoxide, magnesiumethoxide, magnesiumpropoxide, magnesiumbutoxide, magnesiumphenoxide, ethylethoxymagnesium, methoxymagnesium chloride, ethoxymagnesium chloride, phenoxymagnesium chloride, aluminumtrimethoxide, aluminumtriethoxide, aluminumpropoxide, aluminumtriphenoxide, diethylaluminummethoxide, ethylaluminumdiethoxide, diphenoxyaluminum chloride, ethoxyaluminum dichloride, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, tetraphenoxysilane, tetratolyloxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, diethyldiethoxysilane, trimethoxychlorosilane, dimethoxydichlorosilane,

dimethoxydibromosilane, methoxytrichlorosilane, diethoxydibromosilane, dicyclopentoxydiethylsilane, diethoxydiphenylsilane, tris(triphenylsilyloxy)methane, and phenyldihydromethoxysilane, monohydric or dihydric alcohol such as methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, pentyl alcohol, hexyl alcohol, octyl alcohol, ethylene glycol, 1,3-propanediol, glycerin and pentaerythrite, and phenols such as phenol, cresol, resorcin, pyrogallol, and hydroquinone. In particular, alcohol, phenols, siliconalkoxides and aluminumalkoxides are preferred.

In implementing the present invention, only one material may be used for each of electron donor compound (A), magnesium dihalide, titanium compound, electron donor compound (B), [all of which are used to make up catalyst constituent (A)], catalyst constituent (A), an organo-aluminum compound, an organic carboxylic acid ester and a compound containing an M-O-R group. Alternatively, 2 or more compounds may be used together for each of the above.

(i) Usage Amounts

In implementing the present invention, the usage amount of catalyst constituent (A) is in general 0.0001 to 1 atom equivalent of titanium atoms per mole of an organo-aluminum compound. More preferably, the usage amount is 0.0005 to 0.5 atom equivalent of titanium atoms per mole of an organo-aluminum compound. In particular, much more preferably, the usage amount is 0.001 to 0.2 atom equivalent of titanium atoms.

Moreover, the usage amount of a compound having an M-O-R group and/or oxygen is in general 0.02 to 2.0 moles per mole of an organo-aluminum compound. More preferably, the usage amount is 0.05 to 1.0 mole per mole of an organo-aluminum compound. In particular, much more preferably, the usage amount is 0.05 to 0.8 mole. When 2.0 moles or more of a compound having an M-O-R group and/or oxygen is used per mole of an organo-aluminum compound, then the obtained catalyst would exhibit a degraded polymerization activity and hence, it is not desired.

Furthermore, the usage amount of an organic carboxylic acid ester is in general 0.01 to 1.0 mole per mole of an organo-aluminum compound. More preferably, the usage amount is 0.05 to 0.8 mole per mole of an organo-aluminum compound. In particular and much more preferably, the usage amount is 0.05 to 0.5 mole. When 1.0 mole or more of an organic carboxylic acid ester is used per mole of an organo-aluminum compound, then not only an obtained catalyst would exhibit a degraded polymerization activity, but also the activity loss during a polymerization process would be large. Hence, it is not desired.

In addition, from the view point of the three-dimensional specificity of an obtained catalyst, the total amount of a compound having an M-O-R group, oxygen and an organic carboxylic acid ester shall be in general 0.05 to 3.0 times that of an organo-aluminum compound. Preferably, the total amount should be 0.05 to 2.0 times that of an organo-aluminum compound. Much more preferably, the total amount should be 0.1 to 2.0 times that of an organo-aluminum compound.

Moreover, the usage amount of an organic carboxylic acid ester is in general 0.05 to 20 moles per mole of a compound having an M-O-R group and oxygen. More preferably, the usage amount is 0.2 to 20 moles per mole of a compound having an M-O-R group and oxygen. When 50 moles or more of an organic carboxylic acid ester is used per mole of a compound having an M-O-R group and oxygen, then an obtained catalyst would exhibit a three-dimensional specificity and hence, it is not desired. On the other hand, the usage amount of 0.05 mole or less is not desired because the activity highly degrades during a polymerization process.

(j) Polymerization Method of Olefins

There are no restrictive conditions for the supply methods of each catalyst constituent to a polymerization vessel, except that no water should exist at all and each should be supplied in an inert gas environment (e.g., nitrogen). (However, there are exceptions in which water or oxygen is used when a compound having an M-O-R group is supplied.) Each of the catalyst constituents may be separately supplied, or two or more constituents may make contact with each other in advance. However, it is desired that catalyst constituent (A) and a compound having an M-O-R group and/or oxygen and/or an organo-aluminum compound, or an organic carboxylic acid ester and an organo-aluminum compound are not kept in contact for a long period of time because such contact will induce a degradation in catalyst performances.

Moreover, a compound having an M-O-R group and an organo-aluminum compound may make contact with each other in advance, so that a portion of the reaction product which is soluble in a hydrocarbon is extracted and used.

A catalyst which is obtained in a method as described above polymerizes olefins having at most 12 carbon atoms. Representative examples of such olefins are ethylene, propylene, butene-1, 4-methylpentene-1, hexene-1, and octene-1. In implementing the present invention, one of these olefins may be homopolymerized, or two or more of these olefins may be copolymerized (e.g., copolymerization of ethylene and propylene).

A polymerization reaction can be carried out in either an inert solvent, a monomer liquid (olefin), or a gas phase. Moreover, a molecular weight adjustment agent (in general, hydrogen) may be present at the same time in order to obtain polymers with a practical degree of melt flow.

A temperature for polymerization is in general -10 to 180 degrees Celsius. More practically, it is room temperature to 130 degrees Celsius.

In other aspects such as the form of a polymerization vessel, a control method of polymerization, and a method of a post-polymerization process, there are no restrictions specific to the catalysts of the present invention. All known methods are applicable.

[VI] Examples and Comparison Examples

Hereinbelow, the present invention is explained in more detail using examples.

In these Examples and Comparison Examples, the heptane index (in other words, H.R.) expresses the remaining amount in % after extracting the obtained polymers with boiling n-heptane. The melt flow index (in other words, MFI) was measured according to JIS K-6758-1968 and the melt index (M.I.) was measured according to JIS K-6760. The flexural rigidity and tensile yield strength are measured according to ASTM D-747-63 and ASTM D-638-64T, respectively, using a press piece which is obtained according to JIS K-6758-1968.

Each of the compounds (e.g., organic solvents, olefins, hydrogen, titanium compounds, magnesium dihalides, organic compounds having an M-O-R bond, and electron donor compounds) which were used to produce catalyst constituents and polymers essentially did not have a water content. Moreover, productions of catalyst constituents and polymers were carried out essentially without the presence of water content. They were performed under a nitrogen environment.

[(A) Production of Each Catalyst Constituent]

Anhydrous magnesium chloride 20 grams (0.21 mole) (which is prepared from commercially available anhydrous magnesium chloride by drying the material under heat in a dry nitrogen flow at approximately 500 degrees Celsius for 15 hours) and electron donor compound (A) were put in a vibration ball mill vessel, wherein electron donor compound (A) was benzoyl chloride (hereafter, called compound (a)), tetraethoxysilane (hereafter, called compound (b)) or ethyl benzoate (hereafter, called compound (d)), and each of them was used for the quantity specified in Table 1-1. (The

vibration ball mill vessel has a cylindrical shape and an internal volume of 1 liter, and is made of stainless steel. Ceramic balls with an inner diameter of 10 mm were placed in the vessel until the balls appeared to occupy approximately 50% of the internal volume.) The vessel then was attached on a vibration ball mill. At an amplitude of 6mm and vibration frequency of 30Hz, the materials were crushed together for 8 hours. Out of the obtained uniformly crushed powder, each material combination 15 grams was placed in a 500 ml flask. Then, one of solutions was added therein. The solutions were prepared in advance by mixing and reacting a titanium compound and electron donor compound (B) for the amount specified in Table 1-1 at 70 degrees in 125 ml of toluene. The titanium compound was titanium tetrachloride (TiCl_4) or titanium tetrabromide (TiBr_4). Electron donor compound (B) was triphenyl phosphite (hereafter, called "compound (c)"), diphenylphosphochloridate (hereafter, called "compound (e)"), dimethyldimethoxysilane (hereafter, called "compound (f)"), phenylmethylpolysiloxane (viscosity at 25 degrees Celsius: 450 centistokes) (hereafter, called "compound (g)"), anisole (hereafter, called "compound (h)"), or compound (a). Each mixture was stirred for 2 hours at 70 degrees Celsius. (As for Example No. 6, a reaction product of TiCl_4 and tetratolyloxysilane (hereafter, called "compound (?)") was added to a crushed mixture of magnesium and compound (a). The amounts of magnesium and compound (a) in the crushed mixture is specified in Table 1-1. The amount of each mixture is also specified in Table 1-1. The amount of compound (?) was one quarter of TiCl_4 in mole ratio.) The obtained solid portions were separated through filtration and washed in toluene (heptane in Example 5) until titanium tetrachloride or titanium tetrabromide was no longer observed in the filtrates. After washing, the materials were dried under reduced pressure at 40 degrees Celsius. Thus, catalyst constituents in a powder form were prepared. The titanium content of each of the obtained catalyst constituents is shown in Table 1-1.

[(B) Polymerization of Propylene and Produced Polymers (Physical Properties of Propylene)]

One of the catalyst constituents which were obtained by the above methods and one of the solutions were placed in a stainless steel autoclave having an internal volume of 3.0 liters. In each of the solutions, an organo-aluminum compound, a compound having an M-O-R group, and an organic carboxylic ester compound made contact with each other in advance. (The solvent of the solutions was toluene. The solution concentration was 1 mole/liter of aluminum atoms.) The amount of each material (a catalyst constituent, an organo-aluminum compound, a compound having an M-O-R group, and an organic carboxylic ester compound) is specified in Tables 1-2 No. 1 through 1-2 No. 7. An

organo-aluminum compound was triethylaluminum $\text{Al}(\text{C}_2\text{H}_5)_3$, or triisobutylaluminum $\text{Al}(\text{i-C}_4\text{H}_9)_3$. A compound having an M-O-R group was compound (b), tetramethoxysilane (hereafter called "compound (i)"), ethyl alcohol (hereafter called "compound (j)"), water (hereafter called "compound (k)"), oxygen (hereafter called "compound (l)"), aluminumtriethoxide (hereafter called "compound (m)"), or magneisumethoxide (hereafter called "compound (n)"). An organic carboxylic ester compound was compound (d), or ethyl anisate (hereafter called "compound (p)"). (As for Examples 58 through 60, $\text{Al}(\text{C}_2\text{H}_5)_3$ and compound (d) were contacted. Five minutes later, the mixture was contacted with compound (b). Then, the mixture was placed in an autoclave with catalyst constituent (I). (The amounts of $\text{Al}(\text{C}_2\text{H}_5)_3$, compound (d), compound (b) and catalyst constituent (I) are specified in Tables 1-2.)) Immediately afterwards, 760 grams of propylene and 0.07 gram of hydrogen were added. (However, as for Examples 25 through 27, 0.02 gram of hydrogen was used instead.) The temperature in the autoclave was increased and the inner temperature (the reaction system) was kept at 70 degrees Celsius. Each combination underwent a polymerization process for a duration specified in Tables 1-2. Afterwards, the internal gas was removed and the polymerization was terminated. As a result, polymers (polypropylene) in a white powder form were obtained. The yields are summarized in Tables 1-3 No. 1 through No. 7. Productivity for each of the obtained polymers was calculated from the corresponding yield. The productivity and H.R. for each polymer are shown in Tables 1-3.

Then, each powder material was used without a special purification process. Each of them 100 parts in weight was mixed with a stabilizing agent 0.15 parts in weight, distearylthiopropionate 0.20 parts in weight, and calcium stearate 0.10 parts in weight in a pusher machine as the mixture was pushed to form pellets under a nitrogen environment at 210 degrees Celsius. The pusher machine had an inner diameter of 20mm and a ratio L/D of 40. The stabilizing agent was tetrakis(methylene-3-(3'5'-di-tert-butyl-4'-hydroxyphenyl)propionate)methane (Irganox 1010 by Chiba Gaigie). The obtained pellets showed the same degree of whiteness and transparency as those of what are commercially available. The MFI of pellets of each material is shown in Tables 1-3. Moreover, the flexural rigidity and tensile yield strength of pressed plates made from each pellet of Examples 1 through 3 and Comparison Examples 1 through 3 are shown in Table 1-3, No. 1.

Table 1-1

Example No.	Electron donor compound (A)		Titanium compound		Electron donor compound (B)		Catalyst constituent	
	Material	Usage amount (moles)	Material	Usage amount (moles)	Material	Usage amount (moles)	Titanium atom content (% in weight)	Abbreviation
Example 1	Compound (a)	0.043	TiCl ₄	0.45	Compound (?)	0.23	1.8	Catalyst constituent (I)
Example 2	Compound (a)	0.043	TiCl ₄	0.45	Compound (?)	0.27	2.4	Catalyst constituent (II)
Example 3	Compound (a)	0.043	TiCl ₄	0.45	Compound (g)	0.45	2.0	Catalyst constituent (III)
Example 4	Compound (a)	0.043	TiCl ₄	0.45	Compound (h)	0.45	3.8	Catalyst constituent (IV)
Example 5	Compound (a)	0.043	TiCl ₄	0.45	Compound (q)		2.5	Catalyst constituent (V)
Example 6	Compound (b)	0.022	TiCl ₄	0.45	Compound (a)	0.45	8.1	Catalyst constituent (VI)
Example 7	Compound (c)	0.075	TiCl ₄	0.45	Compound (a)	0.45	1.9	Catalyst constituent (VII)
Example 8	Compound (b)	0.022	TiCl ₄	0.45	Compound (a)	0.45	1.6	Catalyst constituent (VIII)
Example 9	Compound (d)	0.040	TiCl ₄	0.45	----	----	2.5	Catalyst constituent (IX)
Example 10	Compound (a)	0.043	TiBr ₄	0.45	Compound (?)	0.23	2.0	Catalyst constituent (X)
Example 11	----	----	TiCl ₄	0.45	Compound (?)	0.23	1.1	Catalyst constituent (XI)

Table 1-2 No. 1

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Example 1	Catalyst constituent (I)	30.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 2	Catalyst constituent (I)	31.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 3	Catalyst constituent (I)	33.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 1	Catalyst constituent (I)	30.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 2	Catalyst constituent (I)	33.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 3	Catalyst constituent (I)	31.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120
Example 4	Catalyst constituent (II)	40.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 5	Catalyst constituent (II)	44.0	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 6	Catalyst constituent (II)	39.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 4	Catalyst constituent (II)	38.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 5	Catalyst constituent (II)	43.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 6	Catalyst constituent (II)	39.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120

Table 1-2 No. 2

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Example 7	Catalyst constituent (III)	31.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 8	Catalyst constituent (III)	30.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 9	Catalyst constituent (III)	25.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 7	Catalyst constituent (III)	30.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 8	Catalyst constituent (III)	32.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 9	Catalyst constituent (III)	29.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120
Example 10	Catalyst constituent (IV)	33.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 11	Catalyst constituent (IV)	31.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 12	Catalyst constituent (IV)	30.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 10	Catalyst constituent (IV)	30.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 11	Catalyst constituent (IV)	32.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 12	Catalyst constituent (IV)	27.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120

Table 1-2 No. 3

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Example 13	Catalyst constituent (V)	53.0	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 14	Catalyst constituent (V)	55.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 15	Catalyst constituent (V)	52.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 13	Catalyst constituent (V)	53.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 14	Catalyst constituent (V)	56.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 15	Catalyst constituent (V)	52.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120
Example 16	Catalyst constituent (VI)	44.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 17	Catalyst constituent (VI)	42.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 18	Catalyst constituent (VI)	38.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 16	Catalyst constituent (VI)	40.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 17	Catalyst constituent (VI)	41.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 18	Catalyst constituent (VI)	39.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120
Example 19	Catalyst constituent (VII)	77.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 20	Catalyst constituent (VII)	71.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 21	Catalyst constituent (VII)	70.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120

Table 1-2 No. 4

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Poly- meri- zation duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Comparison Example 19	Catalyst constituent (VII)	73.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	30
Comparison Example 20	Catalyst constituent (VII)	70.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	60
Comparison Example 21	Catalyst constituent (VII)	68.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.46	---	---	120
Example 22	Catalyst constituent (VIII)	38.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	30
Example 23	Catalyst constituent (VIII)	35.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	60
Example 24	Catalyst constituent (VIII)	31.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	120
Comparison Example 22	Catalyst constituent (VI)	37.0	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	2.2	---	---	30
Comparison Example 23	Catalyst constituent (VIII)	34.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	2.2	---	---	60
Comparison Example 24	Catalyst constituent (VIII)	32.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	2.2	---	---	120
Example 25	Catalyst constituent (IX)	21.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.24	Compound (b)	1.44	30
Example 26	Catalyst constituent (IX)	21.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.24	Compound (b)	1.44	60
Example 27	Catalyst constituent (IX)	20.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.24	Compound (b)	1.44	120
Comparison Example 25	Catalyst constituent (IX)	21.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.36	---	---	30
Comparison Example 26	Catalyst constituent (IX)	21.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.36	---	---	60
Comparison Example 27	Catalyst constituent (IX)	20.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.36	---	---	120

Table 1-2 No. 5

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Example 28	Catalyst constituent (X)	36.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	30
Example 29	Catalyst constituent (X)	32.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	60
Example 30	Catalyst constituent (X)	31.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.96	Compound (b)	1.44	120
Comparison Example 28	Catalyst constituent (X)	33.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.95	---	---	30
Comparison Example 29	Catalyst constituent (X)	31.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.95	---	---	60
Comparison Example 30	Catalyst constituent (X)	30.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	1.95	---	---	120
Example 31	Catalyst constituent (VI)	32.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	Compound (b)	1.44	30
Example 32	Catalyst constituent (I)	30.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	Compound (b)	1.44	60
Example 33	Catalyst constituent (I)	29.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	Compound (b)	1.44	120
Example 34	Catalyst constituent (I)	33.3	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 35	Catalyst constituent (I)	32.0	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 36	Catalyst constituent (I)	30.8	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Example 37	Catalyst constituent (I)	31.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (I)	1.44	30
Example 38	Catalyst constituent (I)	29.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (I)	1.44	60
Example 39	Catalyst constituent (I)	28.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (I)	1.44	120

Table 1-2 No. 6

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Example 40	Catalyst constituent (l)	20.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (j)	2.16	30
Example 41	Catalyst constituent (l)	17.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (j)	2.16	60
Example 42	Catalyst constituent (l)	13.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (j)	2.16	120
Example 43	Catalyst constituent (l)	21.5	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (k)	2.6	30
Example 44	Catalyst constituent (l)	18.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (k)	2.6	60
Example 45	Catalyst constituent (l)	12.0	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (k)	2.6	120
Example 46	Catalyst constituent (l)	23.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (l)	1.0	30
Example 47	Catalyst constituent (l)	17.4	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (l)	1.0	60
Example 48	Catalyst constituent (l)	13.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (l)	1.0	120
Example 49	Catalyst constituent (l)	22.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (m)	0.70	30
Example 50	Catalyst constituent (l)	17.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (m)	0.70	60
Example 51	Catalyst constituent (l)	13.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (m)	0.70	120
Example 52	Catalyst constituent (l)	30.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (n)	1.0	30
Example 53	Catalyst constituent (l)	30.2	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (n)	1.0	60
Example 54	Catalyst constituent (l)	28.9	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.72	Compound (n)	1.0	120

Table 1-2 No. 7

Example No. Or Comparison Example No.	Catalyst constituent		Organo-aluminum compound		Organic ester compound		Compound containing an M-O-R group		Polymerization duration (min)
	Material	Usage amount (mg)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	Material	Usage amount (millimole)	
Comparison Example 31	Catalyst constituent (I)	31.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	---	---	30
Comparison Example 32	Catalyst constituent (I)	31.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	---	---	60
Comparison Example 33	Catalyst constituent (I)	28.8	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (p)	0.64	---	---	120
Comparison Example 34	Catalyst constituent (I)	32.4	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	1.48	---	---	30
Comparison Example 35	Catalyst constituent (I)	30.7	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	1.48	---	---	60
Comparison Example 36	Catalyst constituent (I)	29.3	$\text{Al}(\text{i-C}_4\text{H}_9)_3$	4.8	Compound (d)	1.48	---	---	120
Comparison Example 37	Catalyst constituent (I)	29.7	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	---	---	Compound (b)	1.92	120
Example 55	Catalyst constituent (I)	32.0	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	30
Example 56	Catalyst constituent (I)	30.3	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	60
Example 57	Catalyst constituent (I)	30.1	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120
Comparison Example 38	Catalyst constituent (XI)	43.6	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.8	Compound (d)	0.48	Compound (b)	1.44	120

Table 1-3 No. 1

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)	Rigidity (10^3 kg/cm^2)	Tensile yield strength (kg/cm^2)
		(gram/gram of catalyst constituent)	(kg/gram of Ti)				
Example 1	168	5,563	309	96.4	12.3	14.1	338
Example 2	314	9,905	550	96.2	13.6	14.0	334
Example 3	452	13,573	754	96.5	13.0	14.1	337
Comparison Example 1	239	7,760	431	96.2	5.3	13.4	328
Comparison Example 2	331	9,764	542	96.3	3.0	12.9	321
Comparison Example 3	319	10,257	570	96.0	4.1	12.8	317
Example 4	152	8,791	158	98.1	11.5	---	---
Example 5	265	6,023	251	98.0	10.6	---	---
Example 6	347	8,852	369	98.8	13.8	---	---
Comparison Example 4	201	5,221	218	97.9	4.2	---	---
Comparison Example 5	282	6,543	273	98.2	3.5	---	---
Comparison Example 6	273	6,877	287	98.3	3.2	---	---

Table 1-3 No. 2

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Example 7	193	6,146	307	95.3	12.9
Example 8	292	9,511	476	95.0	11.6
Example 9	390	13,684	684	94.8	10.8
Comparison Example 7	222	7,208	360	94.4	3.9
Comparison Example 8	296	9,193	460	94.2	3.4
Comparison Example 9	294	10,068	503	94.2	4.5
Example 10	141	4,234	111	95.7	10.1
Example 11	223	7,102	187	95.8	12.7
Example 12	330	10,680	281	95.4	13.6
Comparison Example 10	166	5,515	145	96.8	5.1
Comparison Example 11	242	7,401	195	97.5	4.2
Comparison Example 12	225	8,094	213	96.5	3.9
Example 13	167	3,009	120	95.6	11.5
Example 14	278	5,009	200	95.2	11.8
Example 15	358	7,362	294	95.1	13.0

Table 1-3 No. 3

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Comparison Example 13	168	3,164	127	94.5	4.3
Comparison Example 14	239	4,208	168	94.2	3.7
Comparison Example 15	230	4,406	176	94.2	3.4
Example 16	87	1,955	24	97.6	10.8
Example 17	129	3,050	38	97.3	11.3
Example 18	186	4,794	59	97.4	12.2
Comparison Example 16	113	2,776	34	97.7	3.8
Comparison Example 17	130	3,168	39	97.9	3.7
Comparison Example 18	141	3,562	44	97.2	3.2
Example 19	109	1,401	74	94.0	13.5
Example 20	164	2,294	121	94.0	12.7
Example 21	158	2,248	118	93.7	13.1
Comparison Example 19	120	1,628	86	94.4	5.0
Comparison Example 20	151	2,139	113	94.1	5.4
Comparison Example 21	157	2,279	120	94.0	4.7

Table 1-3 No. 4

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Example 22	106	2,775	173	97.4	12.8
Example 23	165	4,661	291	97.7	13.6
Example 24	218	6,995	435	97.2	13.1
Comparison Example 22	144	3,892	243	97.4	4.3
Comparison Example 23	167	4,855	303	97.5	4.4
Comparison Example 24	158	4,922	308	97.4	5.5
Example 25	113	5,280	211	92.1	4.4
Example 26	179	5,483	339	91.7	6.5
Example 27	248	12,216	489	91.3	7.1
Comparison Example 25	135	6,221	249	91.9	5.2
Comparison Example 26	162	7,606	304	91.8	6.6
Comparison Example 27	172	8,515	422	91.4	7.3
Example 28	136	3,736	186	97.2	14.1
Example 29	194	6,019	301	97.4	13.8
Example 30	279	8,774	439	97.5	13.2

Table 1-3 No. 5

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Comparison Example 28	169	5,015	251	97.3	5.7
Comparison Example 29	197	6,254	313	97.8	6.0
Comparison Example 30	205	6,634	332	97.6	5.1
Example 31	151	4,646	258	96.8	13.1
Example 32	229	7,608	423	97.0	12.2
Example 33	335	11,279	627	97.0	13.7
Example 34	172	5,165	287	93.4	12.0
Example 35	285	8,906	495	93.2	13.1
Example 36	390	12,662	703	93.6	11.3
Example 37	197	6,176	343	95.2	12.8
Example 38	291	9,864	548	95.7	11.4
Example 39	423	15,000	833	95.2	13.5
Example 40	160	7,921	440	92.5	6.7
Example 41	208	12,023	668	92.2	4.7
Example 42	269	19,779	1099	92.3	7.8

Table 1-3 No. 6

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Example 43	143	6,651	369	92.7	5.3
Example 44	223	12,120	673	92.7	6.2
Example 45	234	19,500	1,083	92.2	4.9
Example 46	136	5,862	326	92.8	7.1
Example 47	175	10,057	559	93.0	6.2
Example 48	211	15,746	875	93.1	5.8
Example 49	117	5,177	288	95.3	5.6
Example 50	150	8,772	487	94.9	6.5
Example 51	171	12,895	716	95.1	6.7
Example 52	152	5,017	279	95.6	7.4
Example 53	251	6,311	462	95.3	5.2
Example 54	370	12,803	711	95.4	5.9
Comparison Example 28	163	5,241	291	96.2	5.2
Comparison Example 29	208	6,645	369	96.0	4.8
Comparison Example 30	202	7,014	390	95.7	4.2

Table 1-3 No. 7

Example No. Or Comparison Example No.	Yield of polymers (gram)	Productivity		H.R. (gram)	MFI (gram/10 min.)
		(gram/gram of catalyst constituent)	(kg/ gram of Ti)		
Comparison Example 34	204	5,296	350	93.3	5.4
Comparison Example 35	244	7,948	442	93.1	3.6
Comparison Example 36	245	8,362	465	93.1	3.9
Comparison Example 37	431	14,522	807	88.3	13.5
Comparison Example 38	187	4,289	390	84.6	11.9
Example 55	155	4,844	151	96.6	12.9
Example 56	282	9,307	307	96.3	13.1
Example 57	390	12,957	430	96.4	12.8

Examples 58 ~ 60 and Comparison Examples 39 ~ 41

[Homopolymerization of Ethylene and Physical Properties of each of the Obtained Polymers]

Catalyst constituent (I), $\text{Al}(\text{C}_2\text{H}_5)_3$ 0.55 gram (4.8 millimoles), compound (d) 0.07 gram (0.48 millimole) and compound (b) 0.30 gram (1.44 millimole) were put in a 3.0-liter stainless steel autoclave. The amount of Catalyst constituent (I) is shown in Table 2. (However, as for Examples 39 through 41, compound (d) 0.22 gram (1.46 millimole) was used instead of compound (b).)

Furthermore, isobutane (as an inert solvent) 1.0 kg and hydrogen 0.19 gram were added to each combination. After the temperature in the autoclave was increased to 85 degrees Celsius, ethylene was supplied while maintaining the temperature. While the ethylene partial pressure was maintained at 10 atmospheres (by a pressure reading on a gauge), polymerization was performed for 30, 60 or 120 minutes. Then, the gas content was removed and the polymerization was terminated. Yields of the obtained polymers (polyethylene) in a powder form and the productivity calculated from the yield of each polymer (polymer yields per gram of catalyst constituent (I) and per gram of titanium atoms in catalyst constituent (I)) are shown in Table 2.

Each powder material was used without a special purification process. Each of them 100 parts in weight was mixed with a stabilizing agent, 2,6-di-tert-butyl-4-methyl-phenol, 0.2 parts in weight in a pusher machine as the mixture was pushed to form pellets under a nitrogen environment at 180 degrees Celsius. The pusher machine had an inner diameter of 20mm and a ratio L/D of 40. The obtained pellets showed the same degree of whiteness as that of those which are commercially available. The M.I. of pellets of each material is shown in Table 2.

Examples 61 ~ 63 and Comparison Examples 42 ~ 44

[Comopolymerization of Ethylene and Butene-1, and Physical Properties of each of the Obtained Polymers]

In Examples 61 through 63 and Comparison Examples 42 through 44, ethylene and butene-1 were copolymerized for 30, 60 and 120 minutes using the same conditions as described in Examples 58 through 60 and Comparison Examples 42 through 44, respectively, except that the usage amount of catalyst constituent (I) was as shown in Table 3, triisobutylaluminum 0.95 gram (4.8 millimoles) was used instead of an organo-aluminum compound of $\text{Al}(\text{C}_2\text{H}_5)_3$, and furthermore, 16.0 grams of comonomer, butene-1, coexisted for the copolymerization. Yields of the obtained copolymers (copolymers of ethylene butene-1) in a powder form and the productivity calculated from the yield of each copolymer (copolymer yields per gram of catalyst constituent (I) and per gram of titanium atoms in catalyst constituent (I)) are shown in Table 3.

Using the same method as described in Examples 58 through 60, pellets were produced by a pusher machine as the mixture was stirred. Each obtained pellet showed the same degree of whiteness as that of those which are commercially available. The M.I. of each of the obtained copolymers and the number of ethyl groups per 1,000 carbon atoms ($\text{C}_2\text{H}_5/1,000 \text{ C}$) are shown in Table 3.

Table 2

Example No. Or Comparison Example No.	Usage amount of catalyst constituent (I) (mg)	Polymerization duration (minute)	Yield of polymers (gram)	Productivity		M.I. (gram/10 min.)
				(A) ¹⁾	(B) ²⁾	
Example 58	128	30	207	1,617	90	1.8
Example 59	104	60	291	2,798	155	1.5
Example 60	97	120	420	4,330	241	1.6
Comparison Example 39	122	30	288	2,361	131	0.85
Comparison Example 40	108	60	319	2,954	164	0.77
Comparison Example 41	105	120	333	3,171	176	0.74

- 1) gram/gram of catalyst constituent (I)
- 2) kg/gram of Ti

Table 3

Example No. Or Comparison Example No.	Usage amount of catalyst constituent (I) (mg)	Polymerization duration (minute)	Yield of polymers (gram)	Productivity		M.I. (gram/10 min.)	C ₂ H ₅ /1000C
				(A) ¹⁾	(B) ²⁾		
Example 61	125	30	212	1,694	94	1.9	4.4
Example 62	103	60	295	2,864	159	2.0	4.2
Example 63	90	120	401	4,456	248	1.7	4.7
Comparison Example 42	109	30	231	2,119	118	0.92	3.9
Comparison Example 43	115	60	294	2,557	142	0.81	3.8
Comparison Example 44	92	120	244	2,652	147	0.77	4.3

- 1) gram/gram of catalyst constituent (I)
- 2) kg/gram of Ti

Examples 64 ~ 66 and Comparison Examples 45 ~ 47

[Comopolymerization of Propylene and Ethylene, and Physical Properties of each of the Obtained Polymers]

In Examples 64 through 66 and Comparison Examples 45 ~ 47, propylene and ethylene were copolymerized using the same conditions as described in Examples 1 through 3 and Comparison Examples 1 through 3, respectively, except that the usage amount of catalyst constituent (I) was as shown in Table 4, and ethylene comonomer was introduced at a rate of 1.2 grams/5 minutes for the copolymerization. Yields of the obtained copolymers and the productivity calculated from the yield of each copolymer (copolymer yields per gram of catalyst constituent (I) and per gram of titanium atoms in catalyst constituent (I)) are shown in Table 4. Moreover, pellets were made using each of the obtained copolymers in the same manner as described in section (B) of Example 1. The MFI value of each pellet is shown in Table 4.

Table 4

Example No. Or Comparison Example No.	Usage amount of catalyst constituent (I) (mg)	Polymerization duration (minute)	Yield of polymers (gram)	Productivity		M.I. (gram/10 min.)
				(A) ¹⁾	(B) ²⁾	
Example 64	30.5	30	176	5,770	321	14.8
Example 65	31.2	60	309	9,904	550	13.7
Example 66	32.4	120	436	13,457	748	13.1
Comparison Example 45	32.6	30	254	7,791	433	5.5
Comparison Example 46	33.3	60	325	9,760	542	6.2
Comparison Example 47	30.2	120	311	10,298	572	6.0

1) gram/gram of catalyst constituent (I)

2) kg/gram of Ti

Propylene was polymerized using the same conditions as those in Example 1, except that the amounts of used hydrogen were as shown in Table 5. For these experiments, the catalysts in Examples 1 and 4, Comparison Example 38, and a reference example were used. (In the reference example, AA-

type titanium trichloride 0.20 gram and diethylaluminum chloride 0.58 gram were used.) Table 5 shows the H.R. of each of the obtained propylene materials in a powder form and the MFI values of the pellets which were made from these powder materials using the same conditions as described in Example 1.

Table 5

Symbol in Figure 1	Example No.	Catalyst	Usage amount of hydrogen (gram)	H.R. (%)	MFI (gram/10 min.)
(A)	1	Example 1	0.07	96.2	13.6
	2		0.03	96.4	5.1
	3		0.012	96.0	1.4
	4		0	96.4	0.22
(B)	5	Example 4	0.07	98.0	10.6
	6		0.03	98.1	5.7
	7		0.012	98.4	1.0
	8		0	97.8	0.23
(C)	9	Comparison Example 38	0.07	84.2	12.1
	10		0.03	83.7	5.3
	11		0.012	88.0	1.3
	12		0	88.5	0.48
(D)	13	Reference Example	0.12	89.1	8.2
	14		0.07	91.5	1.8
	15		0.03	92.4	0.40

Figure 1 shows the relationship between the H.R. of the polypropylene powder materials which were obtained using the catalysts shown in Table 5 and the MFI of the corresponding pellets.

Figure 1 clearly shows that the H.R. hardly varies even as the MFI is increased when polypropylene materials were obtained through polymerization processes using the catalysts of the

present invention, while the H.R. drastically degrades for higher MFI values when polypropylene materials were obtained through polymerization processes using the catalysts of Comparison Example 38 and the reference example.

4 Brief Explanation of Figures

Figure 1 shows the relationship between the H.R. of the polypropylene powder materials which were obtained using the catalysts of Examples 1 and 4, Comparison Example 38 and the reference example shown in Table 5 and the MFI of the corresponding pellets. (The units of the vertical and horizontal axes are % and gram/10 minutes, respectively.)

Figure 2 shows the relationship of the productivity against the polymerization duration for Examples 1 through 3 (which are marked as A), Examples 37 through 39 (which are marked as B), Examples 40 through 42 (which are marked as C), and Comparison Examples 1 through 3 (which are marked as D). (The units of the vertical and horizontal axes are productivity of polymers per gram of each catalyst constituent, and minute, respectively.)

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Figure 1

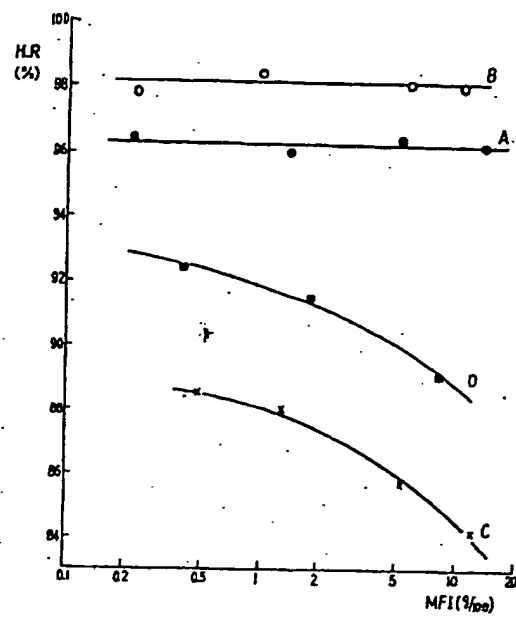
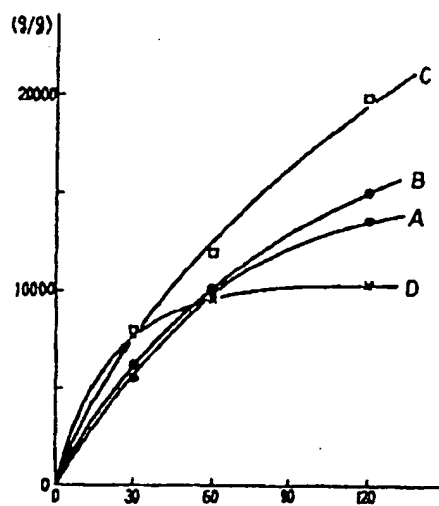


Figure 2

Productivity



Polymerization Duration (minutes)